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LIME SULPHITE FIBER MANUFACTURE IN THE UNITED STATES.

By Major O. E. MICHAELIS, M. Am. Soc. C. E.

WITH

SOME REMARKS ON THE CHEMISTRY OF THE PROCESSES.

By MARTIN L. GRIFFIN, M.A.

WITH DISCUSSION.

A brief account of a comparatively new industry in this country, an industry which in the near future may demand the time, attention, application and talent of hundreds of young American engineers, can hardly fail to possess some interest for the profession, and this consideration must be my apology for presenting a seemingly unscientific paper. It belongs exclusively to the domain of industrial engineering, yet I take it the scope of our Society is broad enough to embrace everything that pertains to material progress and development, not only in engineering science, but also in the arts of manufacture.

An engineer cannot be a school product. The ramifications of the profession, involving every application of scientific truth and mechanical invention to "the uses of man," have in this nineteenth century become too numerous to be even mentioned, far less studied, in any possible technical curriculum. There is only one practical school training for the modern engineer; his education should be so broad, so exact, that, when unexpectedly called upon to enter upon any given unanticipated investigation, construction or manufacture, he can concentrate, crystallize and absorb experience in a minimum space of time; and in our very best engineering schools, this truth controls, perhaps not avowedly, the course of study.

My object in broaching this view is to encourage our bright young graduates, to make them feel that even when foreign methods are in question, as in the manufacture concerning which I write, wherein virtually we are dependent upon cumbersome—I use the word advisedly —talent, a very little study, a very brief experience, will enable them to master the subject, and once mastered, "Improvements in the Manufacture of Sulphite Fiber" will become a familiar caption in the *Patent Gazette*.

Last fall, some acquaintances of mine, desiring to obtain information concerning the manufacture of wood cellulose by the bisulphite process, asked me to make an investigation. Accompanied by Mr. M. L. Griffin, M.A., of Holyoke, Mass., an expert wood-pulp chemist, I visited Alpena and Detroit, Mich.; Appleton and Monico, Wis.; Cornwall, Ontario; Lawrence, Mass., and Birmingham, Conn., at which places the various methods of making sulphite fiber were in actual operation.

Everywhere we were treated with courtesy and consideration, on occasion with generous candor and unreserved openness; indeed, it is not likely that two seekers for knowledge in this branch of manufacture, will ever again have such exceptional facilities extended to them. Reports were made by Mr. Griffin and myself, and the following is in the main the gist of what I reported; Mr. Griffin has kindly supplemented this by some remarks upon the chemical aspects of the subject. As I have in view only the desire to attract the attention of those who may so soon make themselves competent experts, to this opportunity for the remunerative application of their skill, I shall not enter into much detail, but merely give my own impressions as simply and as briefly as possible.

Sulphite fiber, or pure wood cellulose, supersedes rag stock in paper making. The wood, in chips or discs, is boiled in great digesters with a solution of bisulphite of lime, and the main engineering problem lies in the construction of a suitable, economical and lasting digester. The processes examined, in alphabetical order, were the Graham, the Mitscherlich, the Partington, the Ritter-Kellner, and the Schenk.

The investigator is at once struck by the astonishing difference in size and boiling pressure between the Mitscherlich and all the other digesters; the former is 14 x 40 feet, the largest of the latter 10 x 28 feet; the steam gauge on the former registers 40 to 45 pounds, while on all the others, 75 to 80 pounds. Why these differences? The reply to both these suggested questions develops an intrinsic difference of operation between the Mitscherlich and all the other systems. The boiling point of liquids rises with the pressure, and while in all these sulphite processes we have to do with a solution of greater specific gravity than water, for purposes of comparison we can consider the temperature of the boiling point of water. According to Rankine, under a pressure of 40 to 45 pounds water boils at 267 to 275 degrees Fahr.; at 75 to 80 pounds, at 308 to 312 degrees. Hence Mitscherlich boils at about 40 degrees Fahr. lower temperature than the others, consuming, of course, more time for complete conversion, and to compensate, he boils a greater quantity.

Professor Mitscherlich claims that the slower boiling yields a better and surer output. His digester turns out from ten to fourteen tons, the others from one and a half to three tons, at a "boil." He requires for cooking from forty-five to seventy-two hours; the others, from fifteen to twenty-four.

Exteriorly all the digesters are of metal, all of open-hearth steel or iron plate, except the Schenk, which is of so-called deoxidized bronze. All are approximately cylindrical, except the Partington, which is spherical. The cylinders are upright in the Ritter-Kellner and Schenk processes; in the Mitscherlich and Graham they are horizontal. The digesters are fixed, with the exception of the Partington and Graham, which revolve, the Graham about its longer axis.

Upon careful exterior survey of the digesters, I was struck by the fact that both the Partington and Ritter-Kellner were tapped at numerous points, and the holes closed by screw plugs. I learned that the purpose of these vents was to locate leaks; indeed, at Monico these

holes were not closed, and the sulphite solution exuded in perceptible quantity.

Considered merely as a vessel strong enough to stand a given pressure, the only available substance of which the digester can be made, looking from an economical standpoint, is iron or steel. The majority of the digesters are made of rolled iron plates; the Detroit, of open-hearth steel. There is no reason why our gun iron, with a tensile strength approximating 40 000 pounds, should not be available for digesters. They could be turned out in sections ready for assembling; the advantages of such a substitution for the complicated rivet-work shell are evident. At remote inland points the large digesters must be assembled *in situ*, and boilermakers must now be transported for the purpose. A properly handled wrench would suffice to set up the sectional cast-iron construction.

A 14 x 40 feet cast-iron digester has been designed, with a factor of safety of 6, which will cost less than the riveted apparatus, to say nothing of the facility with which it can be transported, and the ease with which it can be assembled by unskilled labor.

We come now to the inside of the digester. Owing to the well known affinity of the bisulphite solution for iron, all digesters made of this metal must be lined with a resistant, fluid-tight material, as a protection against the solvent action of the "acid" mixture. The Schenk digester, a uni-metal construction of deoxidized bronze, is assumed to be sufficiently resistant to the solution without protecting lining. The Graham, Partington and Ritter-Kellner digesters are all lead-lined, the Mitscherlich, fire-brick lined. I use the word "fire-brick" for want of a better. The bricks used are of special form, and are made of a German refractory clay, which seems to me to be about the same as is used in the manufacture of the Nassau Seltzer jugs.

Digester Linings.

The vital point in these sulphite processes lies in the ability of the digester to resist the erosive action of the acid solution and its gaseous products. Lead has for centuries been used as a lining material in the manufacture of sulphuric acid, so that its application to the present sulphite fiber processes lay near at hand. It is used in the Graham, Partington and Ritter-Kellner digesters.

Lead Lining.

In speaking of the sulphite process, the Encyclopedia Britannica uses the following language:

"The pulp or fiber produced by all these processes is of excellent quality, and can be prepared at a cost greatly lower than the soda process. The strength of the fiber is maintained unimpaired even after bleaching, and white paper made solely from such fiber is in every respect superior to that manufactured solely from pulp prepared by boiling with caustic soda.

"Dr. Mitscherlich's process has been extensively adopted in Germany, and there seems little doubt that these processes will in time supplant the use of soda in the case of wood. The great objection to them all is that, as they all depend on the use of bisulphite, which, being an acid salt, cannot be worked in an iron boiler, the boiler must be lined with lead, and great difficulty has been encountered in keeping the lead lining of the boiler in repair."

The primary, indispensable condition in protecting iron sulphite boilers with lead, is that the lining must be continuous—that is, liquid-tight.

Now, lead has a linear co-efficient of expansion much more than double that of iron; in these processes it is subject to a change of temperature of at least 240 degrees Fahr. (300–60 degrees), and the unavoidable resulting flow of the metal cannot be compensated for by permitting sections to expand and to contract freely upon each other, for that would require open joints, a violation of our primary condition. The lead lining must in some way be attached to the iron shell, for otherwise it would soon collapse, or go to pieces in some other way. Only three practical ways offer themselves for the attachment of the lead lining to the iron.

It may be bolted on at proper points; it may be, to borrow a plumber's phrase, "tacked on," at appropriate places, or it may be completely soldered on. The first two methods permit, as is evident, under variations of temperature, changes in the superficial area of the lining; the latter method forcibly resists this, and limits the flow of the lead during the life of the solder union to molecular expression only.

Partington.

This boiler, it will be remembered, is spherical; the lead is applied in spherical lunes, clamped to the iron, and burned to each other. The theory is that it is an easy matter to replace an injured section, and thus to keep the lining intact at comparatively little cost. At Monico, the vents in the shell, already spoken of as "leak locators," were all open, and,—the descriptive aptness of the words would be appreciated by any eye witness,—*in eruption*. Having had some experience in lead burning, I noticed at Monico extensive preparations for conducting it, and, in answer to my inquiries on the subject, the genial and capable superintendent admitted that he had had great trouble with the lining.

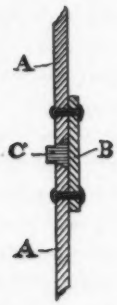
Indeed, the visible débris and the evident condition of the boilers were cogent evidence. It is needless to make further comment; "he who runs, may read" is here applicable. I learn that since my visit these boilers have been destroyed by fire, and have been replaced by another construction. At Lawrence, where a battery of eight Partingtons is in operation, the digesters were certainly more presentable; but there I observed that the usual hand apparatus for lead burning was apparently not considered sufficient, for the manager had applied an installation furnished with a power pump, and a system of conducting air and hydrogen pipes *in situ* at each boiler.

It is evident that in the Partington digester, the lunes must bulge from the iron under expansion, and must again be forced into contiguity under contraction and pressure. Hence, there is periodic "flapping," which, it seems to me, must in time result in fissuring. Of course, constant watchfulness and timely burning would prevent destructive results upon the shell. The expense of this can only be inferred from the statements made in regard to the cost of the output. Neither at Monico, nor at Lawrence, was an opportunity offered to make an interior examination. At Monico, such examination would have been merely a work of supererogation.

The Ritter-Kellner.

The digester, about 10 x 28 feet, is built up of cylindrical sections, 4 feet wide, a few inches apart, and fastened by heavy exterior bands. The object of this construction is to provide the means for attaching the lead lining peculiar to this process.

The spaces between these sections form annular dovetail mortises thus:



A.—*Boiler Shell.*
B.—*Exterior Band.*
C.—*Annular Tenon of Lead and Antimony Alloy.*

These mortises are filled with an alloy of lead and antimony, and at the ends of a diameter meet similar vertical tenons, to which they are attached. The lining is burned fast to this semi-cylindrical frame. Here, again, under the irresistible force of expansion, these great sheets of lead, roughly speaking 16 x 4 feet, must theoretically, if the tacking holds, "pucker up," and again be forced back against the shell under contraction and pressure.

Again, it seems to me that this constant movement to and fro must, in the end, bring about fissuring. At Cornwall we were told no trouble of this kind has been experienced, and the digester we entered, more than half filled with chips, showed no evidence of degradation detectable in the very brief time at our disposal.

I asked two bright prominent officials, one of the parent, the other of the Canadian company, "What becomes of the increased superficial area due to the difference in the expansion of the iron and lead?" One said he didn't know and had no theory on the subject, the other replied: "This is no longer a matter of theory, it is an accomplished success."

The digester is, however, provided with abundant vents, or leak locators, and in reply to my question regarding their practical value, the gentleman in charge explained to me that by using a pneumatic pump the noisy issue of the air through the nearest vent located the leak. This was so graphically told, that I was at once convinced the description was founded upon auricular observation.

The Graham.

The Graham digester, 7½ x 22 feet, is made of sheets of boiler plate, to which the lead lining is soldered before bending and assembling. The method of doing this is ingenious and simple.

The sheet is cleansed, and smoothed by a radially traveling emery wheel; it is then firmly fixed for half its surface over a gas-jet heater. The rectangular frame that holds it down is packed with fire-proof packing where it rests upon the plate, thus actually forming a water-tight vessel, of which the iron to be leaded is the bottom. The plate is copiously doused with a solution of chloride of zinc, and when heated to the proper degree molten lead in sufficient quantity is poured upon it.

Although the promoters of this process do not so call it, it is, nevertheless, soldering, which is authoritatively defined to be "the process of uniting two pieces of the same or of different metals by the interposition of a metal or alloy, which, by fusion, combines with each."

Here the metals to be united are lead and iron; the "metal or alloy" is zinc, or zinc and lead. I emphasize this simple matter because it is claimed that in the Graham process the two metals are united by a special alloy of lead and iron.

I quote from the company's courteous, well posted expert:

"Our boiler obviates these defects and overcomes the difficulties and repairs and constant inspection to which ordinary lead lined boilers are liable. This is because the lead is united to the iron or steel uniformly by means of an alloy at the point of junction between the steel and lead, and the crystals of the two metals are intimately mixed at the point, so much so that it is impossible with a cold chisel to cut the lead away from the iron or steel without still leaving a thin surface of lead. The junction alloy of steel and lead has also a greater breaking strain than lead itself, it having been subjected to breaking tests."

A standard authority states that "an alloy is a combination by fusion of two or more metals, as brass and zinc, tin and lead, silver and copper, etc." Hence to speak of "the junction alloy of steel and lead" is incorrect, for in the coating operation there is not even an approximation to the melting point of iron.

The alloy of lead and iron appears to be almost unknown in the arts; and that this so-called "junction alloy of steel and lead," or, as I think, of zinc and lead, should possess a greater tensile strength than the lead,

is not strange, it is not an unusual property of alloys; thus one consisting of 12 parts lead and 1 part zinc has six times the tenacity of lead.

I must also put on record my lack of faith in the natural inference that would be drawn from the claim that the two metals (iron and lead) are intimately mixed at this point (the junction or cementation surface), "so much so that it is impossible with a cold chisel to cut away from the iron or steel without still leaving a thin surface of lead." Under favorable circumstances the lead can be "peeled" from the iron—I have done it myself.

I examined the Graham process after the Ritter-Kellner at Cornwall, and it struck me at once as a logical consequence that if "tacking" the lead on in places only gave satisfactory results, then complete cementation ought to do even better. Upon reflecting, however, I modified this hasty conclusion—for the governing conditions in the two processes are entirely different. In the Ritter-Kellner the lead is burned to the circular and vertical tenons.

Burning is defined as "joining metals by melting their adjacent edges, or heating the adjacent edges and running into the intermediate space some molten metal of the same kind." A well known writer says:

"The articles burned together being homogeneous, the parts expand and contract evenly by changes in temperature; the solders have a greater range of expansion by given changes of temperature than the metals they connect.

"The solders oxidize more or less freely than the metals they connect, and establish galvanic circuits which destroy the integrity of the joint, especially in the presence of heat, moisture or acids."

One would almost suppose the author had sulphite digesters in mind.

In the Ritter-Kellner there is little danger of the joints loosening. In the Graham, under periodic expansion and contraction and galvanic action, I should fear a sundering between the lead and iron; if this did take place the boiler would very soon become unserviceable. Even granting the claim that the lining and sheet are indissolubly connected by an alloy of lead and steel, and that the "lead, being the weaker metal, when fastened homogeneously to the iron or steel, has to obey the expansion and contraction of the iron or steel," there still remains an apparently insuperable difficulty. The lead lining is at least half an inch

thick, and even supposing that the cylindrical laminæ in homogeneous contact with the iron are docile, and move in military cadence with their inseparable stronger companion, yet the balance of the lead must be subjected to a recurring ebb and flow for which no compensation is provided. I quote from the Graham expert:

"The explanation of the iron controlling the lead expansion is easy to understand. Lead is a very malleable metal, its crystals fitting loosely together, *i. e.*, there is comparatively a large space between the crystals as against other metals, and if the crystals of lead were counted over 22 feet (the length of the digester), and the number divided into one-third of an inch (the linear expansion of lead for 90 degrees in 22 feet), it would be found that the fractional part of this one-third inch would be considerably less than the space between each crystal, and there is no chance of one crystal pushing another one, as in metals where crystals are closer together."

On this theory I do not understand why lead should expand measurably under ordinary increase of temperature. Further, the common experience of every plumber militates against the correctness of the assumption.

Lead pipes for hot water will "creep" under fluctuation of temperature without perceptible increase of length; this is very evident when the pipe under a metallic clamp is examined; a burnished band is seen protruding beyond the clamp. I have seen this in less than twenty-four hours after brand-new pipes were installed.

It is a well known fact that in hotels, for instance, where a large quantity of hot water is used in the morning and very little during the rest of the day, the pipes being thus subjected to frequent and comparatively great changes of temperature, this very movement of which I have spoken, to use plumbers' parlance, "kills" them. That is, they lose all elasticity, become brittle and crack, showing a crystalline fracture. Now, I am inclined to think that there is danger of such a result with the lead lining of the Graham boiler, even if the cementation remain intact. The lead, under this constant, enormous molecular stress, will degrade, become brittle, porous, crack, even drop off. (See Note 1.)

Then the boiler is ruined, for the lining, under such circumstances, can neither be repaired nor replaced.

Although I have not seen the patents issued to the Graham Company, yet I am of opinion that they can afford but slight protection.

The lead coating of iron has long been well known in the arts, as seen in terne plates, and no modern patent can limit the amount of lead that may be applied.

Brick Lining.—The Mitscherlich.

The Mitscherlich digester, as already stated, is lined with an acid-proof brick of special design, laid in Portland cement.

Apparently a startling innovation, reflection proves that this method follows out the direct line of modern progress. The manufacture of that almost indispensable article, sulphuric acid, has in comparatively late years been greatly improved and facilitated by the introduction of the Gay-Lussac and Glover towers, edifices lined, not with lead, but with acid-proof tiles or brick. It is a curious coincidence, in this connection, that about seven years ago one of the leading American sulphuric acid makers told me that he had found that Seltzer jugs made the most resistant tower linings. The transition from brick-lined towers to brick-lined digesters must have been no difficult task for so able a scientist as Dr. Mitscherlich.

The ability of fire-clay to withstand enormous stresses is familiar to us all. The Bessemer Converter and the Open-hearth furnace are illustrations in point.

The co-efficient of expansion of fire-brick is only about 40 per cent. that of iron; in a length of 40 feet for a change of 180 degrees Fahr. a fire-brick construction would expand linearly less than one-quarter of an inch. Mortised and tenoned together, due to the special form of brick used, and laid in Portland cement, it constitutes a homogeneous mass, whose integrity is not jeoparded by usual fluctuations of temperature.

I have examined, with the utmost care, digesters that have been in use for nearly two years, and have failed to discover any intrinsic defect in the lining. The best steam boiler imaginable is liable to blow up if not handled with ordinary care, and so doubtless must an average degree of watchfulness be exercised in the use of the Mitscherlich, as well as of any other digester. An absolutely automatic digester, that fills, cooks, empties and cleans itself, is still an undiscovered desideratum. The cement joints are now and then superficially percolated by the acid solution; they give clear warning of this percolation by discoloration; a cold chisel to cut out the affected mortar, and a trowel to repoint with cement, afford a ready, inexpensive, efficacious remedy.

In one of the digesters I noticed a patch back of one of the upper man-holes. The cause of the corrosion was very apparent, and its occurrence inculcated a valuable lesson. The man-hole is lined with lead, this is "bent under," flanging well back of the intersection of the man-hole cylinder with the digester. The brick lining comes up to this well, and, of course, has an open circular junction line, which must be kept well pointed, as at present constructed. This was neglected, the liquid penetrated, followed the lead, and ate its way through the iron. Such an accident can only occur under long continued, persistent neglect.

I know of no engineering objection to a brick or tile lining for a low pressure digester. Such constructions, as already stated, do withstand extremes of temperature; indeed, on the Continent air-tight tile stoves are in general use.

Unlined Digesters.—The Schenk.

The Schenk digester is a stationary, upright cylinder, 7 feet in diameter by 22 feet height, and is made in sectional castings of deoxidized bronze with planed flanges, which are bolted together and lead-jointed in assembling. This alloy the designer assumes is sufficiently acid-proof for the purpose, without the protection of other resistant lining.

Absolutely homogeneous kalchoid alloys are not of usual occurrence in manufactures; liquation, the presence of copper oxides, and the occlusion of gas, militate against the production of constant results. I take it that "deoxidized" bronze is the outcome of a process that hopes for uniform, reliable castings.

The value of phosphor-bronze in the arts is well established, and it is used in all the lead-lined digesters for the steam inlets that are immersed in the acid solution. In every case these inlet pipes are in time consumed.

I am not prepared to admit, after such examination as I have been able to make, that deoxidized bronze is superior as an acid resistant to phospor-bronze. From the little that I have gleaned, it is claimed that it casts more surely in large masses. Even from this standpoint, aluminium-bronze will probably be found to be more reliable.

I mention phosphor and aluminium bronze because there is no patent *per se* upon the Schenk digester; the only protection claimed lies in the fact that the company enjoys the exclusive right of making digesters of deoxidized bronze; hence, should any other copper alloy

be found equally available for the purpose, no impediment exists to its free use.

It is acknowledged that the deoxidized bronze is acted upon by the acid solution, and observation confirms this conclusion.

The upper portion of the digester, the only part that could be examined on account of the chip filling, was coated with black oxide of copper, and both liquid and fiber hold it in solution or suspension.

It is claimed that this erosion is so slight that the longevity of the digester is not threatened thereby; this, of course, is a matter of individual opinion.

The digester we entered at Appleton showed extensive and deep honeycombing in the throat; we were told that this was due to bad casting. Without this information I should have come to a very different conclusion.

As I understood, one of the claimed valuable attributes of deoxidized bronze is that it makes sound castings.

It hardly seems judicious to use so unsound a section in an entirely new apparatus, designed as the foundation of a great manufacture. The pittings looked to me like the usual erosions manifested when corroding liquids or gases move over bronze surfaces.

Owing to liquation, more soluble alloys occur in spots, and the eating-out of these produces the typical pitting.

The base section of this digester either had been, or was to be, replaced; the top section I would call in unserviceable condition; at both these places the bronze is exposed, in blowing-off, to moving liquid and gas.

Copper-tin alloys are "kittle-cattle," all authorities agree in testifying to their sensitiveness. (See Note 2.) Fluctuations in temperature affect their strength, and their constant exhibition under active circumstances in the presence of sulphur compounds, cannot fail to produce deleterious effects. (See Note 3.)

It certainly is not customary in permanent engineering constructions, built to withstand continuing, constant strains, to use material that is subject to uncontrolled, cumulative, indefinite wear or abrasion.

Acid Process.

The manufacture of the bisulphite solution may be classified under three heads: The Vacuum Process, the Modified Tower Process, the Tower Process.

I will dwell but briefly upon this matter, confining myself to evident features that would impress the average intelligent observer.

The vacuum system is used in connection with the Partington, the Schenk and the Graham processes. It requires large exhaust pumps, a series of tanks arranged vertically in échelon, a lime mixer, etc., and undoubtedly yields with certainty the high solution required. It can unquestionably be used for all the processes. The best plant I saw was at Birmingham, copied from the English Partington, and costing here about six thousand dollars for the entire installation.

The modified tower system in use with the Ritter-Kellner process at Cornwall is a sort of cross between the Mitscherlich tower and vacuum method. The solution is pumped by a battery of pumps into a series of low towers under cover, filled with limestone. It did not strike us as possessing merits over the vacuum method.

The Mitscherlich tower process is in a measure automatic and is certainly the most economical.

The sulphurous acid gas is drawn up the high towers, filled with limestone, by atmospheric draft, and therein meets water trickling through the filling. Its main disadvantage is the assurance of proper draft. It strikes me that the application of a little American engineering skill would speedily bring about reliable and satisfactory results.

The consumption of sulphur varies from 200 pounds per ton of fiber in the Mitscherlich, up to nearly 600 pounds in the others. In none of the others is it less than 350 to 400 pounds.

Mechanical Preparation of the Wood.

All the processes, except the Mitscherlich, use chips. In this latter, discs cut from the log, 1¼ inches deep, are used.

Dr. Mitscherlich claims that these discs afford a stronger fiber, and that more bulk can be put into the digester, than if loosely piled chips were used. One great disadvantage connected with the use of discs, is that even if the finest cross-cut saws are used, circular or band, at least ten per cent. of the wood is wasted in sawdust. Further, more time must be consumed in charging the digester. All this is a mere question of dollars and cents. There is no absolute objection to using chips in the Mitscherlich process; wood would be saved, labor economized, and time of boiling probably shortened. But, it is claimed by the Professor, the output is not so good. Hence, if the better product earns more,

even at the expense of material, labor and time, than the so-called inferior, why of course it would pay to follow Mitscherlich's recommendations. It would not be a very significant item of expense to be prepared to use both discs and chips.

Cooking.

"Cooking," or the treatment of the wood with calcic bisulphite to obtain cellulose, is fully explained by Mr. Griffin. I will merely dwell long enough upon this branch of the subject, therefore, to make my own impressions clear.

There are two methods pursued, a quick and a slow process, applying the words merely to time, and not to output. The first process, which is not under patent protection, is pursued in all the digesters except the Mitscherlich; the second, covered by an American patent, is peculiar to the Mitscherlich.

The quick process requires for a boil strong liquor, high pressure, short time, and yields a small product. The slow process requires a weak liquor, low pressure, long time, but yields from four to eight times greater a product.

The Mitscherlich, aside from every other consideration, appealed to me as being logical and precise; the other struck me as inconsequent and unscientific.

In the Mitscherlich process, the cooking is done by indirect heat, steam pipes; in the other, by direct heat, the condensation of steam. Hence the former method uses a liquor of uniform, the latter one of constantly varying, strength. To illustrate, 2 600 gallons strong liquor entered the Graham digester, a "quick" boiler, 2 000 gallons of condensed steam are added during cooking.

At one quick method plant we learned that it was frequently necessary to add strong sulphite solution while the boiling was actually going on.

If warm baths were prescribed for a patient, I imagine he would protest vigorously against being immersed in boiling water, even if assured that the cold water had been turned on. The application is readily seen.

The quick process, as we gleaned from inquiries at the various plants where it is carried on, requires from fifteen to twenty-four hours for boiling; the Mitscherlich, as shown by the Alpena experience, from

forty-five to seventy-two hours. It will thus be observed that the range of variation, 60 per cent., is precisely the same for both processes. It was noticeable that in certain cases, the best possible conditions of time, temperature, etc., of the quick process were compared with the most unfavorable showing of the slow.

This matter of time is apt to be misleading. The best claimed showing was made by the Graham expert, nine complete "turns" per week, or a single turn in about eighteen hours, producing 1½ tons of fiber.

The best figures for the Mitscherlich are a complete turn in seventy-two hours, producing nearly 10 tons of fiber, four times as long, with over six times the output.

In the Mitscherlich procedure, one operation impressed me as grotesquely un-American. The cooked fiber is washed for ten hours in the digester. This great money-coining apparatus is compelled, for over one-tenth of its time-capacity, to function as an ordinary washing engine. This is simply an accidental part, in my judgment an evidence of bad business management; yet the opponents are not slow in arguing, from the condition imposed by this ill-judged operation, against the whole method.

As cold water is used in this washing, they claim that the temperature of the Mitscherlich digester fluctuates from 40 to 270 degrees Fahr., a range of 230 degrees, while in their process the temperature never falls below 150 degrees, thus giving a range of only 150 degrees.

This objection is met by an obvious practical remedy, saving time, and consequently money—the introduction of separate washing engines.

In confirmation of Dr. Mitscherlich's claim that slow boiling affords a better fiber, I have been told by an experienced soda pulp manufacturer that it was a well-known fact that in this latter process slow boiling yielded a better output.

It is singular that while the sulphite process was the invention of an American, Germany made it a practical success. We are now beginning to take hold of this American idea, but burdened with German methods, and incrusted with Teutonic barnacles.

The most complete quick process plant I saw was at Cornwall; here everything, including even the assembled digesters and the gauges recording pressures in *atmospheres*, was imported. The superintendent told me that he thought the best course had been pursued, that they

had the necessary experience abroad, and so on, and yet I noticed he was modifying his apparatus about as rapidly as he could.

The German adjuncts and methods at Alpena had to be entirely thrown aside, and apparatus and operations developed in our own paper-making industry have been introduced. There is a reason for all this; in Germany labor is phlegmatic, inexpensive. I have been told that women sort and inspect chips for twelve and a half cents per day, and of course they have none but wooden ideas. As a consequence, the German manufacturer, absorbing the phlegm of his employees, has both perseverance and patience.

We are quick-witted, we have abundance of perseverance in attaining our ends, but precious little patience in waiting for results. To this I ascribe, in a measure, the allurement which the quick process has for us. We hug the delusion to our hearts that we can produce ten tons just as quickly as one and a half, and mentally eliminate all intervening insurmountable difficulties.

The most German of all the processes is the Mitscherlich, yet I firmly believe that with American business management and American engineering skill, it can be rehabilitated as a genuine American method.

It is idle to catalogue the ponderous, painful steps that still characterize it; there is not one that could not be practically improved. The discs, for instance, are really fed, piece by piece, into the digester; they should be automatically shoveled in by the cart-load.

Astonishing as it may seem, the German engineers turned over the first completed plant and acquiesced in its being run by an energetic American, utterly without experience, who at the same time superintended two saw-mills producing annually some forty million feet! It recalls poor Colonel Sellers' "little side speculations."

To attain the best results, the head of the plant should be a sterling business man, interested pecuniarily in its success, aided by competent assistants in the technical, chemical and engineering departments.

NOTE 1.—It may be of interest briefly to investigate the stress to which the lead coating in the Graham digester is subjected by change of temperature.

The linear co-efficient of expansion of lead is....0.0000158
Its modulus of elasticity..... 720 000

A range of 200 degrees is a very moderate assumption for this process, for it boils at over 300 degrees.

We have, then, the stress $p = .0000158 \times 720\,000 \times 200$
$= 2\,275$ pounds.

The elastic limit of lead is given by Trautwine as 1 100; we see, therefore, that, even after making due allowance for the expansion of the iron shell, the fixed lead is strained beyond its elastic limit. Every plumber, from his own experience, can tell what will result.

NOTE 2.—Mr. Griffin's analysis of the Schenk boiler metal gives:

Copper	91.28
Tin	7.68
Zinc	0.89

In 1877 the British Admiralty determined the effect of heat upon the kalchoid alloys of copper (see *Engineering*, October 5th, 1877).

"The metal was cast in the form of rods one inch in diameter, and composed of five different alloys as follows:

* * * * * * * * * * * * *

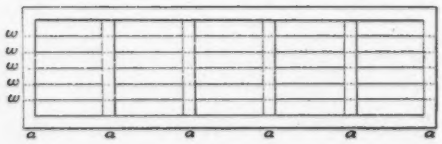
"No. 2.—Copper, 91; Tin, 7; Zinc, 2. (The nearest approach to the Schenk mixture.)

* * * * * * * * * * * * *

"The specimens were heated in an oil bath near the testing machine, and the operation of fixing and breaking was rapidly and carefully performed, so as to prevent, as far as possible, loss of heat by radiation. At 100 degrees Fahrenheit the strength and ductility of the above test piece was 525 pounds and 15.5 per cent. At 300 degrees Fahrenheit the strength was 265 pounds, the ductility nil."

I cite this as confirmatory of my statement regarding the sensitiveness of these alloys.

NOTE 3.—"It is but fair to add here that Professor Langley has observed that acids and the fumes of his laboratory will change the very structure of metals. He had in his laboratory a frame of the following form:



"The wires *w*, of copper, brass and German silver, were run through the crossbars *a*, which were of wood, about 2 inches wide. After three years he noticed the wires breaking, and upon examination he found them to be coarsely crystalline, brittle—in fact, rotten, and entirely changed in structure. He found also that the parts that were in the wood, and so protected from the fumes, were soft, ductile, and entirely unaffected. All of the exposed wires were affected similarly, and all the protected parts were equally unaffected, except the copper wire, which was stiffened, but not materially changed in structure."*

SOME REMARKS ON THE CHEMISTRY OF THE PROCESSES OF LIME SULPHITE FIBER MANUFACTURE.

By Martin L. Griffin, M.A.

I propose in this paper to give an outline simply of the chemistry of the sulphite fiber industry. This will be concerned only with the material for digesters, the bisulphite solution and the fiber.

By sulphite fiber is meant, fiber manufactured from wood for paper making by the use of a solution of bisulphite of lime or magnesia. As you are doubtless aware, the chief difficulty to be overcome in this process is the securing of a digester which will stand the action of the acid solution used to reduce the wood to fiber. I will first explain the composition and nature of this acid liquid. Sulphurous acid gives two classes of salts, like carbonic, the bisulphite and the neutral or normal sulphite. The normal sulphite of calcium has this formula $CaSO_3$, while the bisulphite requires two molecules of the acid radical giving twice as much sulphur and expresses thus:

$$Ca\begin{cases} O\begin{cases} H \\ S=O_2 \end{cases} \\ O\begin{cases} H \\ S=O_2 \end{cases} \end{cases}$$

The former is only soluble in 800 parts of water, though freely soluble in aqueous sulphurous acid, thereby becoming the bisulphites. To

* Steel: its Properties; its Use in Structures and in Heavy Guns. William Metcalf, M. Am. Soc. C. E., Trans. Am. Soc. C. E., Vol. XVI, p. 291, June, 1887.

obtain the solution desired for the manufacture of sulphite fiber we should require for each part of calcium (the ratio of calcium to its oxide, lime, being as 5 to 7) 3.2 parts of sulphurous acid gas or 1.6 parts of sulphur.

This acid solution is made in two principal ways and in all cases the sulphurous gas is produced from burning sulphur in retorts to which only a limited supply of air is admitted. The gases are either received into tall towers, as in the Mitscherlich system, where it is absorbed by porous limestone over which water trickles downward, meeting the ascending gases; or it is absorbed directly into a solution of milk of lime by the aid of a vacuum pump. This is known as the vacuum system. In the former case the sulphurous gas displaces the carbonic, thus: $Ca\,CO_3 + SO_2 = Ca\,SO_3 + CO_2$, and we have the bisulphite solution flowing off. In the latter there is no gas to be displaced, the reaction being $Ca\,(O\,H)_2 + SO_2 = Ca\,SO_3 + H_2O$. By this process a solution of any desired strength can be made.

It may seem to be a very simple operation to burn sulphur to sulphurous oxide; but in reality great care is required, since by the admission of too much air to the retorts sulphuric oxide may be formed. This uniting with the lime forms insoluble sulphate of lime, which in the Mitscherlich towers would form a coating over the limestone and cause a variety of troubles. In the vacuum system it would form an inert deposit, causing a waste of lime and sulphur.

An excess of air will cause the sulphur to burn more rapidly, thus developing too much heat, which facilitates the formation of first lower, then higher, polythionic acids, then sublimed sulphur. These acids are all sulpho-acids having an increasing proportion of sulphur. They not only cause a waste of material, but exert injurious effects upon the quality of the fiber. They also cause a fictitious strength of the liquor which cannot be detected by the ordinary workman.

When we reflect what a peculiar substance sulphur is, and how easily its chemical and physical properties are changed, we cannot wonder that it should cause difficulties in any process in which it is used. At the ordinary temperature sulphur is a light colored brittle solid; at 115 degrees C. it melts to a thin amber liquid; heated to 250 degrees it becomes dark colored and thick; at 450 degrees it boils and passes off as a dark colored vapor. These changes in its state of aggregation are due to changes in the molecule, which varies in the number

of atoms it contains according to the temperature. At 1000 degrees and above it consists of two atoms, at 500 degrees it consists of six atoms, and at lower temperatures it probably contains a still greater number. This peculiarity makes possible a great variety of sulpho-acids and salts. Sulphur is one of the most useful, powerful and peculiar elements with which chemistry deals. Its gases are pungent and penetrating, and its acids the most powerful and corrosive, forming a most stable class of salts. A very small fraction of one per cent. in metals renders them useless and it exerts injurious effects even in the smallest proportions.

Is it any wonder, then, that we should meet with difficulties in finding a material for sulphite digesters? Practically there is only one metal yet discovered which withstands the action of sulpho-acids fairly well; it is lead. A substance very rich in silica is the only mineral. These two kinds of material are all that have accomplished much so far in the construction of sulphite digesters. There are, however, digesters of bronze in operation for which success is claimed. I will now briefly describe those which are doing a representative business.

The Mitscherlich is 14 feet in diameter and 40 feet long, holding about twenty-five cords of wood when cut up into discs 1¼ inches thick and produces at each "turn" 12½ tons of dry fiber. It is composed of a wrought-iron or steel shell ¾ inch thick, which is first coated with pitch or tar within. Upon this is laid a continuous layer of very thin sheet lead; next comes a course of bricks specially made for this purpose, each having a tongue and groove, which are laid flatwise in the best Portland cement. Upon these is laid another course of bricks edgewise, having their tongues and grooves arranged accordingly. Each digester is stationary and placed horizontal.

The Schenk, a bronze digester, has the following composition:

	Per Cent.
Tin	7.68
Copper	91.28
Zinc	0.89

The specific gravity of a small casting was 8.5579; the computed gravity is 8.76. The specific gravity of copper is 8.94. These figures will indicate the difficulty in making perfect castings of copper alloys free from combined and occluded oxygen. Hence it follows that the larger or more numerous the molecular interstices, the more surface is exposed and the more permeable is the metal by gases, and so more

affected. All metals are susceptible to this influence to a greater or less extent. A very marked illustration of the absorption of gas by a metal is observed in the case of palladium, which absorbs 376 volumes of hydrogen at the ordinary temperature.

According, therefore, to the nature of the gas, the metal and the temperature, will various results be observed. I am personally cognizant of a case where lead, under the influence of sulphurous acid gas, has been changed to a salt of this acid. Similar instances are recorded of copper and other metals. Copper when plunged into molten sulphur is immediately changed to the sulphide of the metal.

At the present time we see several manufacturers of bronzes claiming that they have an acid-proof alloy, but no reputable chemist can entertain such an idea for a moment. Neither is any copper alloy proof against the action of sulphurous and sulphuric acids in any proportions. The effect of these acids on digesters of copper alloys is, first, to dissolve a little from the surface, which is immediately reduced to the oxide and sulphide of the metal by the reducing power of the organic matter dissolving from the wood. This soon forms a black coating on the interior, which is continually crumbling off by the expansion and contraction of the metal, thereby contaminating the fiber with black specks. As regards the life of such digesters, it is simply a question of the rapidity of the action of the chemicals and the thickness of the metal. It is not improbable, also, that the scale affords some slight protection to the metal.

We have now left for our consideration digesters lead lined in different ways and of different shapes.

The Ritter-Kellner digester is vertical and stationary, about 10 feet in diameter and 28 feet high, made of wrought-iron or steel, 1 inch thick. The interior is lined with sheet lead half an inch thick. This is attached to horizontal and vertical tenons of lead and antimony dovetailed into the seams. This gives an opportunity for expansion of the lining in sections. The ratio of the expansion of iron to lead is a little less than 1 to 3. As the digester is repeatedly heated and cooled, there must be a recurring movement back and forth from the shell, or else the lining must "buckle." This movement, in time, is sufficient to produce cracks, which then must be repaired. This coincides with experience.

The Partington digester is spherical and rotates upon an axis. It is

built of iron or steel, and the lining of lead is attached in lunes by the use of leaden headed bolts and clamps. This form of attachment has caused more trouble than the others, as the bolts and clamps have offered greater inducements for the liquor to penetrate to the shell, thus requiring more time for repairs by their frequency, and the extra exposure of the shell to injury.

The remaining digester to be described is the Graham. It may be built of any shape or size, stationary or rotary. The chief difference worthy of notice is in the attachment of the lining. In plain language, the lead is soldered to the iron or steel sheets by the aid of chloride of zinc. They are then rolled cold and assembled. The seams are polished and filled in with lead by means of an autogenic apparatus.

The cellulose prepared by all the acid processes contains a considerable quantity of incrustating matter and lime salts, and hence is harsh and brittle. When a magnesian base is used it is claimed that a softer fiber is produced; personally I cannot see much difference. When the pulp is first removed from the digesters it is beautifully transparent, owing largely to the powerful bleaching effect of the sulphurous gas which acts as a deoxidizing agent. Papers made for service for any length of time should be reoxidized and bleached with hypochlorite of calcium. If this is not done, the paper soon assumes a yellow color from exposure to light and air.

The conclusions, therefore, which we draw are: That from a scientific standpoint only two kinds of material are admissible for sulphite digesters. Each must be supported by means of an iron shell. In the one case the lead lining expands much more than its stronger companion, is therefore subject to a great stress, which in time will produce fissures and crystallization, and is permeable by the sulphurous gas, which has a tendency in addition to produce hardness and brittleness. In the other case the brick or tile lining expands much less than the iron shell, and so this is liable also to crack if a temperature above 118 degrees C is reached.

A plant under either of these systems may be successful by good management, nevertheless, without which no enterprise can succeed. Sulphite fiber fills a much needed place in the manufacture of paper and is and will continue to be profitably made.

DISCUSSION.

F. COLLINGWOOD, M. Am. Soc. C. E.—The remarks of Major Michaelis about joining of metals recalls to my mind an experience at one of the American Institute fairs. A substance called the "Cherry-heat Welding Compound" was brought for examination before a committee of which I was a member. It was claimed for it that it produced an absolute weld of steel as strong as could be produced by the ordinary methods, and at so low a temperature as to remove all danger of injury to the steel. As it contained some metallic fragments and also a flux, I asked what the fragments were, and was told they were iron.

To the question whether the introduction of iron between steel surfaces could possibly make a union equal to the steel in strength, the reply was that it certainly did.

I then proposed a test. I was to obtain a weld of two pieces of steel by the old method, and the inventor was to furnish one made by his method from the same bar, this being a fine tool steel.

Each specimen was then turned down to proper size for test in a Thurston's torsional machine, which was conveniently at hand.

The old style of weld broke at the full strengh of the steel directly across the weld, through the solid bar; while that by the new process separated along the welded surfaces, and at about the strength of fair wrought-iron. The so-called weld was really a soldering with iron.

All the experience I have had with soldering bears out Major Michaelis' statements; there is no mystery about it, no fusion or interpenetration of the parts joined. The solder is an alloy of some kind which melts at a lower temperature than the metal soldered, and the higher the temperature is, the more intimate the union, and the stronger is the joint. When the parts joined are both heated to the melting point of the solder, the latter flows, and not before.